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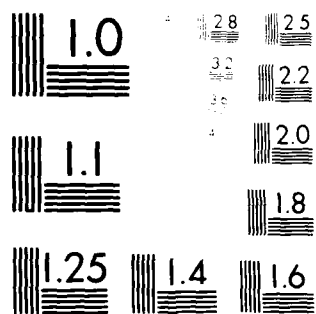
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THE EFFECT OF FERROUS SULFATE ON SULFIDE-INDUCED CORROSION OF
COPPER-BASE CONDENSER ALLOYS IN AERATED SEAWATER

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**DAVID W. TAYLOR NAVAL SHIP
RESEARCH AND DEVELOPMENT CENTER**

Bethesda, Maryland 20084



THE EFFECT OF FERROUS SULFATE ON SULFIDE-INDUCED
CORROSION OF COPPER-BASE CONDENSER ALLOYS
IN AERATED SEAWATER

by

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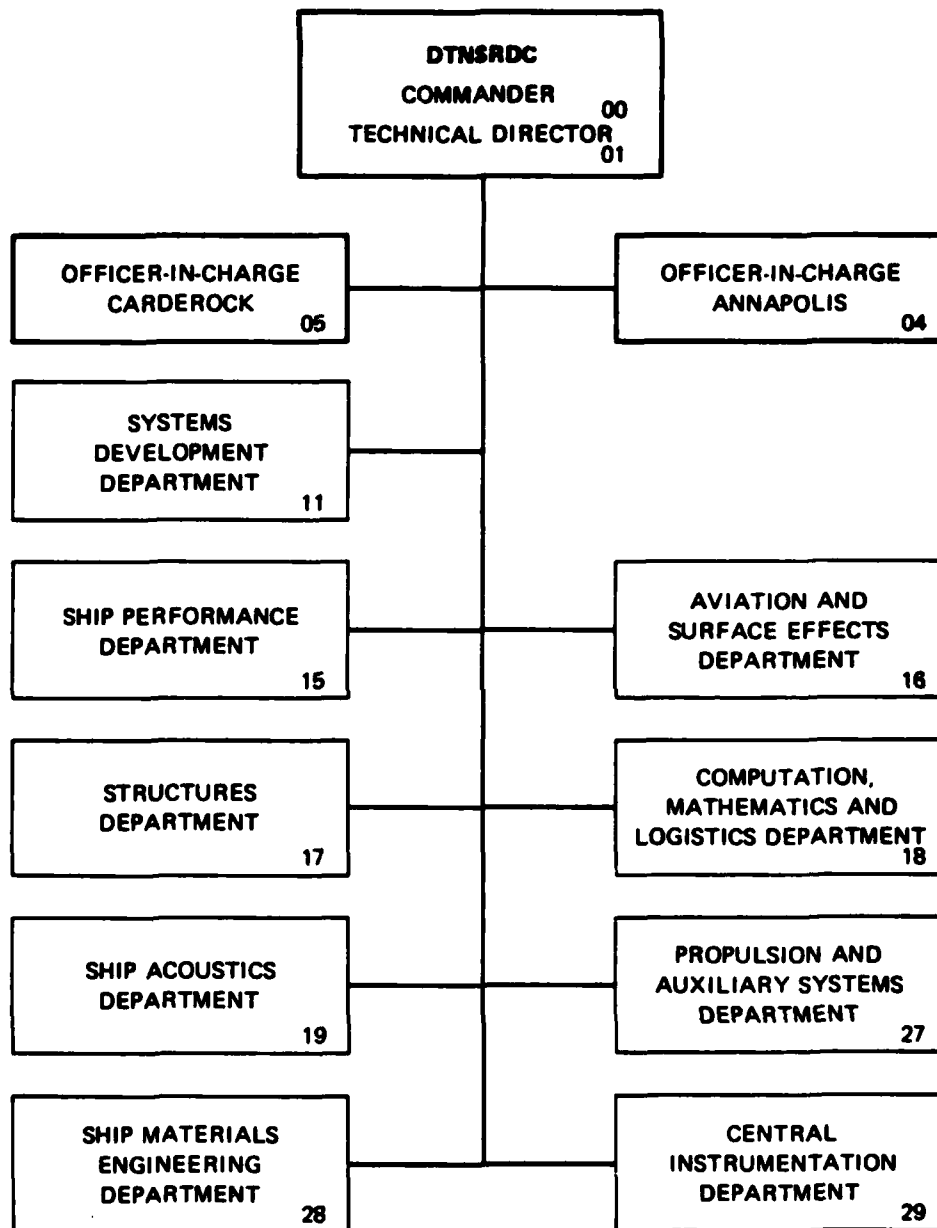
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Exposures were conducted for 30, 60, and 90 days in aerated seawater with and without continuous addition of 0.05 milligram per liter sulfide ion and 0.10 milligram per liter ferrous ions from ferrous sulfate on Alloys C70600 (90-10 copper-nickel), C71500 (70-30 copper-nickel), C72200 (85-15 copper-nickel plus chromium), and C68700 (aluminum brass). All alloys were susceptible to sulfide-induced corrosion. The ferrous sulfate was sufficient to completely counteract the sulfide-induced corrosion of all alloys except Alloy C72200.		

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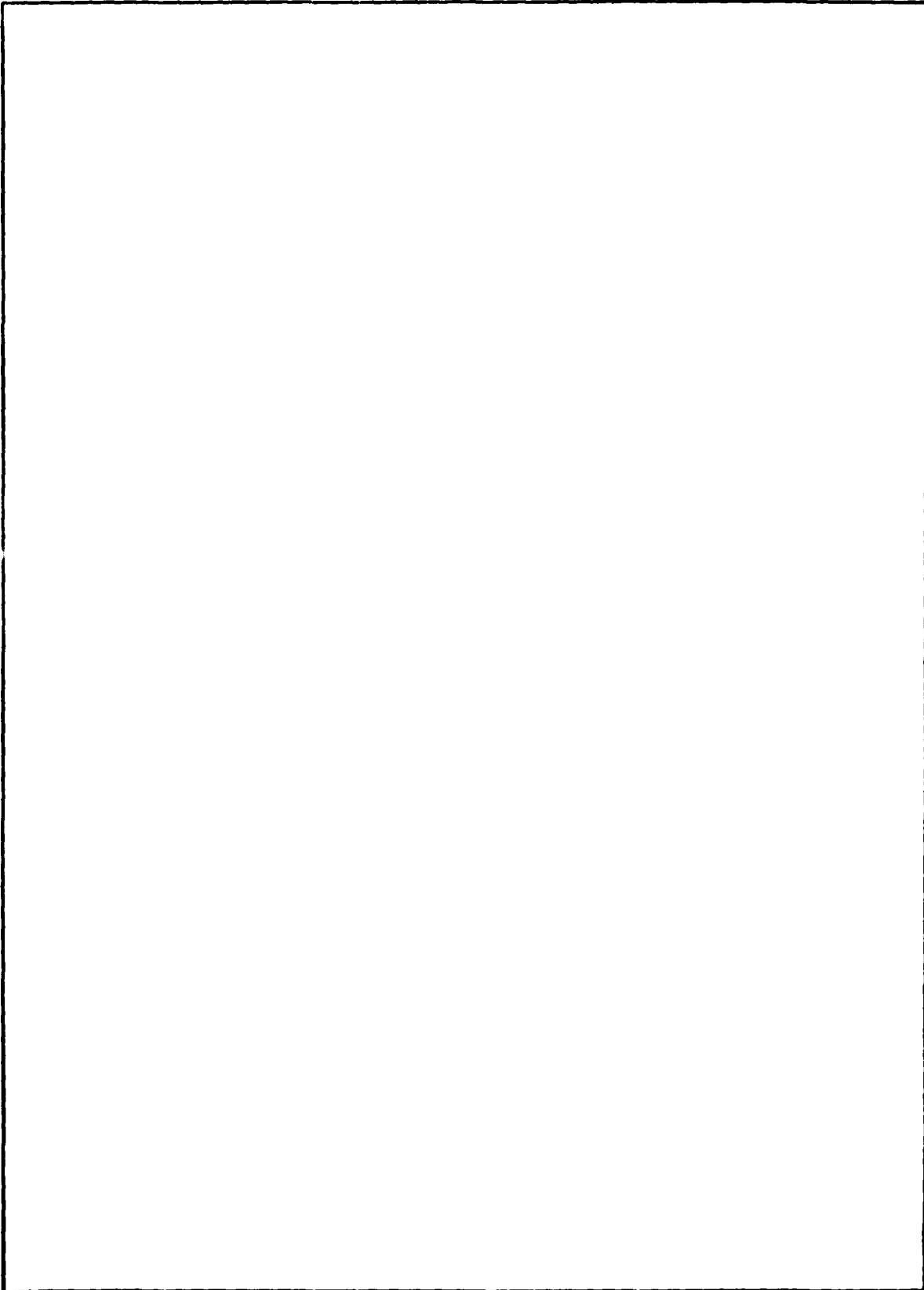
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LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
Avg	Average
$^{\circ}\text{C}$	Degrees Celsius
mg	Milligram
mg/l	Milligram per liter
mm	Millimeter
mm/yr	Millimeters per year
m/s	Meters per second
PVC	Polyvinyl chloride
std dev	Standard deviation
wt %	Weight percent

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ABSTRACT

Exposures were conducted for 30, 60, and 90 days in aerated seawater with and without continuous addition of 0.05 milligram per liter sulfide ion and 0.10 milligram per liter ferrous ions from ferrous sulfate on Alloys C70600 (90-10 copper-nickel), C71500 (70-30 copper-nickel), C72200 (85-15 copper-nickel plus chromium), and C68700 (aluminum brass). All alloys were susceptible to sulfide-induced corrosion. The ferrous sulfate was sufficient to completely counteract the sulfide-induced corrosion of all alloys except Alloy C72200.

ADMINISTRATIVE INFORMATION

This project was partly funded under the Submarine Materials Technology Block Program (Program Element 62761N, Task Area SF61541-591, Work Unit 1-2803-140) sponsored by the Naval Sea Systems Command (SEA 05R15, Dr. H. H. Vanderveldt). This report meets in part milestone RD1.3/4 of the program.

INTRODUCTION

Copper alloys have a long history of successful application in marine environments. This is primarily due to their inherently good corrosion resistance, resistance to fouling by marine organisms, and useful mechanical properties. The characterization and development of copper alloys have been extensively investigated over the years.^{1-5*} It has been shown that their corrosion resistance is attributable to the formation of a protective corrosion product film. In seawater, the predominant component of this film, independent of alloy composition, is cuprous oxide (Cu_2O).^{6,7}

In some applications, corrosion resistance of copper alloys has been further enhanced by the addition of iron to the seawater.⁸⁻¹⁶ This iron has been introduced either through addition of ferrous sulfate or by direct oxidation of an iron "waster piece" using an externally applied current.

North and Pryor⁶ conducted experiments on copper in sodium chloride solutions to demonstrate the mechanism by which ferrous sulfate additions to the environment provide enhanced corrosion resistance.¹⁴ Their work indicated that a surface film

* A complete list of references appears on page 17.

consisting primarily of lepidocrocite ($\gamma\text{-FeO}\cdot\text{OH}$) was formed which acted as a cathodic inhibitor. It was postulated that the lepidocrocite was electrophoretically deposited either directly from a $\gamma\text{-FeO}\cdot\text{OH}$ colloid which formed in solution or through an intermediate step, where ferrous ions are transported to cathodic areas where they are ultimately oxidized to lepidocrocite. In either case, North and Pryor suggested that the film deposition occurred at cathodic sites with the film reducing oxygen transport to the cathode, thereby increasing the rate of cathodic polarization and reducing corrosion. Schrader¹⁷ has also documented the beneficial effect of iron-containing surface films on copper alloys.

Gasparini, *et al*,¹⁵ built upon the work of North and Pryor by investigating the colloidal chemistry involved with ferrous sulfate in demineralized water, river water, and seawater.¹⁵ In natural waters of near neutral pH, it was suggested that the direct formation of lepidocrocite in solution is favored due to both the pH and the presence of dissolved oxygen. They postulated that the protective film formation proceeds directly from the electrophoretic transport of the lepidocrocite from solution to the metal surface. Based on an analysis of zeta potentials, they concluded that the lepidocrocite would be attracted to a Cu_2O surface film, and that the cathodic behavior of the metal surface would not be essential to the film deposition mechanism.

Recent work by Epler and Castle¹⁶ on identification of protective films on aluminum brass condenser tubes has confirmed the presence of a lepidocrocite film on tubes treated with ferrous sulfate. In this instance, the lepidocrocite was postulated to control the rate of diffusion of ions to an underlying Al-Mg-Zn hydroxide layer and thereby enhance the protective nature of the hydroxide layer.

The presence of sulfide in seawater has been demonstrated to have an accelerating effect on corrosion of copper alloys.¹⁸⁻²² This can occur during exposure in deaerated, sulfide-containing seawater followed by exposure in oxygenated seawater or during exposure in aerated seawater containing low levels of sulfide in a nonequilibrium state. While specific levels of pollution in seawater may limit the utility of copper alloys, there is evidence that iron additions to seawater can reduce the extent of sulfide-induced corrosion of selected alloys.²³⁻²⁵

Hack and Gudas^{23,24} previously demonstrated the use of ferrous sulfate (both intermittently and continuously added to seawater) and the use of a stimulated iron anode to reduce sulfide-induced corrosion of copper-nickel (Cu-Ni) Alloys C70600 and C71500. All methods were beneficial in reducing the degree of corrosion

induced by low levels of sulfide in aerated seawater, although limited success was obtained with intermittent dosing with ferrous sulfate to combat corrosion induced by higher, transient levels of sulfide.

Sato²⁵ demonstrated that aluminum brass tubing which was exposed for 1 month to seawater containing 0.03 mg/l* of ferrous ion was more resistant to sulfide-polluted seawater than similar tubing without the ferrous pretreatment.

The studies reported here were conducted to further characterize the behavior of copper-alloy condenser tube materials in seawater when ferrous sulfate is utilized to counteract sulfide-induced corrosion. The sulfide levels chosen were those which had previously been shown to accelerate corrosion of copper alloys, and the ferrous ion levels chosen were those known to reduce corrosion in sulfide-free seawater.

EXPERIMENTAL PROCEDURE

MATERIALS

The alloys investigated in this study were 90-10 Cu-Ni (C70600), 70-30 Cu-Ni (C71500), 85-15 Cu-Ni plus chromium (C72200), and aluminum brass (C68700). The composition of the test materials is presented in Table 1. Each alloy was obtained as wrought, fully annealed sheet in the test thickness and machined to the final length and width for testing. The C72200 material was an experimental heat which may differ slightly in microstructure from the present commercially produced material.

APPARATUS

All exposures in seawater with sulfide or iron additions were conducted in the seawater test apparatus schematically depicted in Figure 1. The apparatus, located at the LaQue Center for Corrosion Technology, Incorporated, at Wrightsville Beach, North Carolina, were constructed of PVC pipe with removable test sections containing specimen holders and sampling points for seawater chemical analyses.

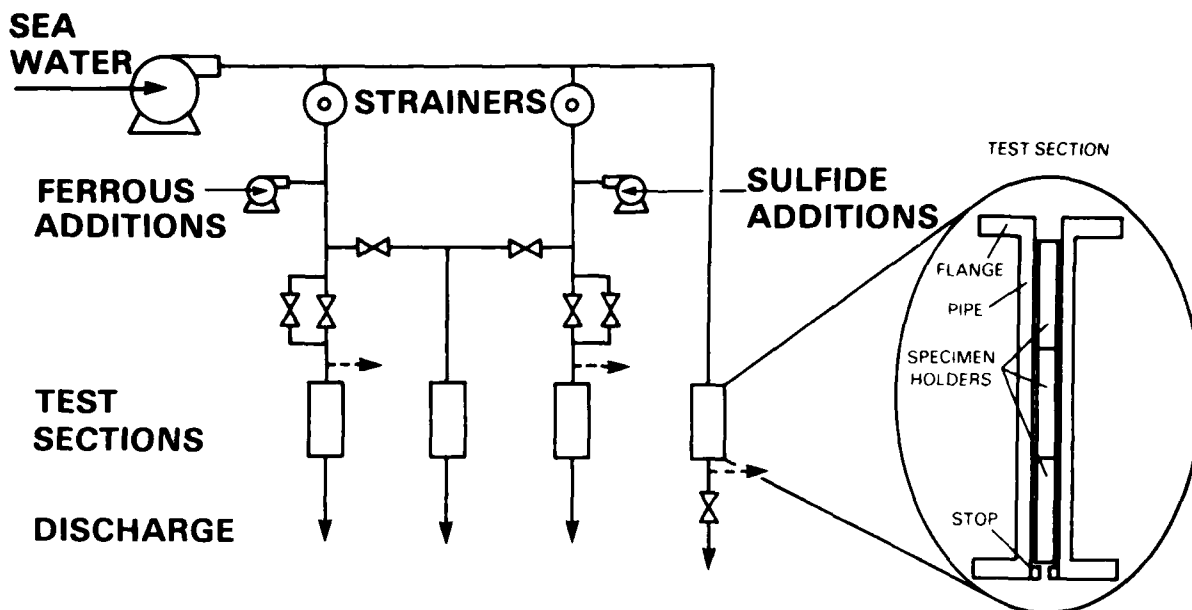
* Definitions of abbreviations used are given on page v.

TABLE 1 - COMPOSITION OF COPPER ALLOYS TESTED

Alloy	Composition (wt %)	
90-10 Cu-Ni (C70600)	0.01	Pb
	1.12	Fe
	0.096	Zn
	<0.02	P
	9.7	Ni
	0.25	Mn
	<0.02	S
70-30 Cu-Ni (C71500)	29.7	Ni
	0.52	Fe
	0.4	Mn
	0.002	Pb
	0.001	P
	0.007	S
	0.06	Zn
85-15 Cu-Ni + Cr (C72200)	0.001	C
	0.80	Mn
	15.9	Ni
	0.63	Cr
	0.002	S
	0.83	Fe
	0.009	P
Al Brass (C68700)	17.8	Zn
	0.0021	Pb
	0.02	Fe
	2.16	Al
	0.092	As

Each removable test section housed three cylindrical acetal resin specimen holders. Each holder supported eight specimens (1.8 x 16.5 x 0.2 cm) parallel to each other and to the water flow. The specimen edges were untapered so that turbulence would be generated at the leading edges.

Duplicate specimens of each material were exposed for 30, 60, and 90 days in each test environment. Prior to exposure, specimens were degreased, cleaned in 10 wt % H_2SO_4 , pumice-scrubbed, and acetone-degreased. After exposure weight loss determinations were made to the nearest 0.1 mg, and a maximum depth of attack on the boldly exposed surfaces of each specimen was recorded using a point-to-point micrometer (± 0.01 mm). Corrosion and pitting rates were calculated by annualizing the weight loss or attack depth for each of the three test durations.



X CONTROL VALVE AND FLOWMETER
 ---> SAMPLING POINTS

Figure 1 - Modified Seawater Test Apparatus

A seawater velocity of 2.0 m/s was maintained through the test sections by the use of control valves and monitored with flowmeters or weir boxes. The modified seawater apparatus was fitted with two injection pumps for adding controlled amounts of sodium sulfide or ferrous sulfate to the incoming seawater, and chlorine generator units at the discharge to oxidize any remaining sulfide. Environmental test conditions included the following:

1. Seawater only with no additions.
2. Seawater with 0.05 mg/l sulfide ions.
3. Seawater with 0.10 mg/l ferrous ions.
4. Seawater with 0.05 mg/l sulfide ions and 0.10 mg/l ferrous ions.

A nominal sulfide concentration of 0.05 mg/l was achieved via continuous, metered addition of aqueous sodium sulfide. A concentration of 0.10 mg/l of ferrous ions was maintained by continuous metered additions of aqueous ferrous

sulfate. No detectable pH change was noted during injection of either solution. The conditions existing in the test loops were not at equilibrium for the levels of sulfide and ferrous ions and dissolved oxygen present. Measurements in the loop indicated that under the conditions of the test the sulfide did not completely react with the excess oxygen present, or with the ferrous ions. This condition may be expected to exist where a source of sulfide (e.g., anaerobic need) allows a release of sulfide into an otherwise aerated seawater environment.

Previous research by Effertz and Fichte²⁶ has identified many of the fundamentals involved in the use of ferrous sulfate. They noted the effect of water chemistry (pH, oxygen level, nature of dissolved solids and suspended matter, and temperature) on the time dependence of gamma-FeO·OH colloid formation in natural waters. Their investigations indicated that the maximum efficiency of the ferrous sulfate treatment would be obtained with maximum gamma-FeO·OH colloid formation. In the current work, no specific attempts were made to optimize colloid formation but rather a consistent pattern was followed for the production of the stock ferrous sulfate solution utilized for injection into the seawater. In this regard, a fresh stock solution containing approximately 25 mg/l of ferrous ions was prepared daily using $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ and potable water. The pH varied between 7.2 and 7.4, and the ambient solution temperature varied from 10° to 15°C.

The sulfide and ferrous ion levels in seawater were measured daily using the p-phenylenediamine colorimetric technique (with a turbidity correction) and the bathophenanthroline method, respectively.^{27,28} Seawater temperature and flow were monitored nine times per day during the exposures.

The background levels of sulfide and ferrous ions in seawater were measured at less than 0.001 and 0.02 mg/l, respectively, and the dissolved oxygen content was nominally 80% or greater of the air saturated value for the given seawater temperature. The measured values for the ion concentrations and temperature are summarized in Table 2. The standard deviation of the sulfide and ferrous ion levels are relatively high compared to the mean and indicate the difficulties in controlling injection at these low levels.

TABLE 2 - SUMMARY OF MEASURED SEAWATER TEMPERATURES
AND SULFIDE AND FERROUS ION LEVELS

Exposure Duration (days)	Measured Quantity	Exposure Condition					
		Sulfide Only		Sulfide + Ferrous		Ferrous Only	
		Avg	Std Dev	Avg	Std Dev	Avg	Std Dev
30	Temperature (°C)	10.8	2.0	10.8	2.0	10.8	2.0
	Sulfide (mg/l)	0.049	0.015	0.025	0.012	0	0
	Ferrous (mg/l)	0.017	0.007	0.079	0.027	0.079	0.019
60	Temperature (°C)	9.3	2.4	9.3	2.4	9.3	2.4
	Sulfide (mg/l)	0.053	0.017	0.029	0.011	0	0
	Ferrous (mg/l)	0.019	0.008	0.088	0.035	0.086	0.031
90	Temperature (°C)	9.6	2.5	9.6	2.5	9.6	2.5
	Sulfide (mg/l)	0.051	0.017	0.027	0.011	0	0
	Ferrous (mg/l)	0.019	0.008	0.099	0.051	0.094	0.037

RESULTS

Results of the exposures are summarized in Table 3. An analysis of variance was conducted on corrosion rate and pitting rate data for all materials, and a summary of the statistically significant variables and interactions is included in Table 4.²⁹ The effect of adding ferrous ions on the corrosion and pitting rates was significant in all cases. The effect of adding sulfide was significant in all cases except in the case of the pitting rate of Alloy C71500. Time was a significant factor affecting corrosion rate on Alloys C70600 and C71500 only, and had a significant effect on pitting rates only of Alloy C72200. The sulfide/ferrous ion interaction had a significant effect on the corrosion rate of all materials except C86700 and a significant effect on pitting rates only of C72200 and C68700. All other two-factor interactions and the three-factor interactions were insignificant except for the six cases noted in Table 4.

TABLE 3 - CORROSION DATA FOR COPPER ALLOYS EXPOSED
IN SULFIDE AND/OR FERROUS MODIFIED SEAWATER

Alloy	Sulfide (mg/l)	Ferrous (mg/l)	Corrosion Rate (mm/yr)			Pitting Rate (mm/yr)		
			30 Days	60 Days	90 Days	30 Days	60 Days	90 Days
C70600	0	0	0.067	0.104	0.099	0.60	0.54	0.44
			0.066	0.099	0.098	0.60	0.48	0.48
	0.05	0	0.198	0.146	0.096	0.96	1.86	0.32
			0.175	0.145	0.102	0.84	1.02	0.54
	0	0.10	0.042	0.065	0.033	0.24	0.36	0.08
			0.045	0.037	0.032	0.24	0.24	0.04
	0.05	0.10	0.131	0.120	0.100	0.48	0.18	0.28
			0.134	0.126	0.085	0.72	0.36	0.20
	0	0	0.116	0.167	0.148	1.44	0.78	0.72
			0.112	0.175	0.130	1.56	0.84	0.64
C71500	0.05	0	0.148	0.352	0.326	0.96	1.80	0.64
			0.157	0.346	0.353	0.60	1.02	1.04
	0	0.10	0.027	0.029	0.021	0.12	0.12	0.04
			0.033	0.030	0.020	0.24	0.18	0.16
	0.05	0.10	0.061	0.080	0.078	1.68	0.36	0.28
			0.073	0.065	0.082	0.60	0.36	0.20
C72200	0	0	0.046	0.024	0.020	1.20	0.18	0.12
			0.025	0.030	0.016	0.60	0.60	0.16
	0.05	0	0.392	0.369	0.473	5.76	3.54	2.88
			0.342	0.356	0.412	5.40	5.70	1.92
	0	0.10	0.012	0.012	0.008	0.12	0.18	0.16
			0.012	0.013	0.009	0.36	0.24	0.28
	0.05	0.10	0.077	0.153	0.138	1.92	2.28	1.16
			0.187	0.098	0.145	3.96	0.84	0.75
C68700	0	0	0.058	0.119	0.093	0.24	0.40	0.63
			0.057	0.118	0.089	0.36	0.40	0.52
	0.05	0	0.188	0.217	0.290	3.60	2.40	2.32
			0.176	0.174	0.232	2.28	2.64	1.88
	0	0.10	0.020	0.015	0.010	0.12	0.12	0.04
			0.018	0.017	0.010	0.24	0.12	0.04
	0.015	0.10	0.152	0.157	0.141	1.20	0.48	0.44
			0.128	0.155	0.130	0.84	0.66	0.36

TABLE 4 - STATISTICALLY SIGNIFICANT VARIABLES AND INTERACTIONS
INFLUENCING CORROSION OF COPPER ALLOYS IN SEAWATER
WITH SULFIDE AND/OR FERROUS ION ADDITIONS

Variables and Interactions	Alloy							
	C70600		C71500		C72200		C68700	
	Corrosion Rate	Pitting Rate	Corrosion Rate	Pitting Rate	Corrosion Rate	Pitting Rate	Corrosion Rate	Pitting Rate
Sulfide	0	0	0	Δ	0	0	0	0
Ferrous	0	0	0	0	0	0	0	0
Time	0	Δ	0	Δ	Δ	0	Δ	Δ
Sulfide/Ferrous	0	Δ	0	Δ	0	0	Δ	0
Sulfide/Time	0	Δ	0	Δ	Δ	Δ	Δ	Δ
Ferrous/Time	Δ	Δ	0	Δ	Δ	Δ	0	Δ
Sulfide/Ferrous/Time	0	Δ	0	Δ	Δ	Δ	Δ	Δ
0 Significant at 99%.								
Δ Not significant at 99%.								

The physical significance of these factors and interactions can be more easily visualized by referring to Figures 2 through 5. Some factors or interactions considered insignificant in the overall analysis in Table 4 gain significance in the discussion below when selective data are considered. In these figures, the corrosion or pitting rates for each alloy and test condition are displayed in bar form with the upper portion of each bar divided to illustrate the behavior of both specimens. Thus a feel for the variability as expressed in the analyses of variance can be obtained from the bar charts.

ALLOY C70600

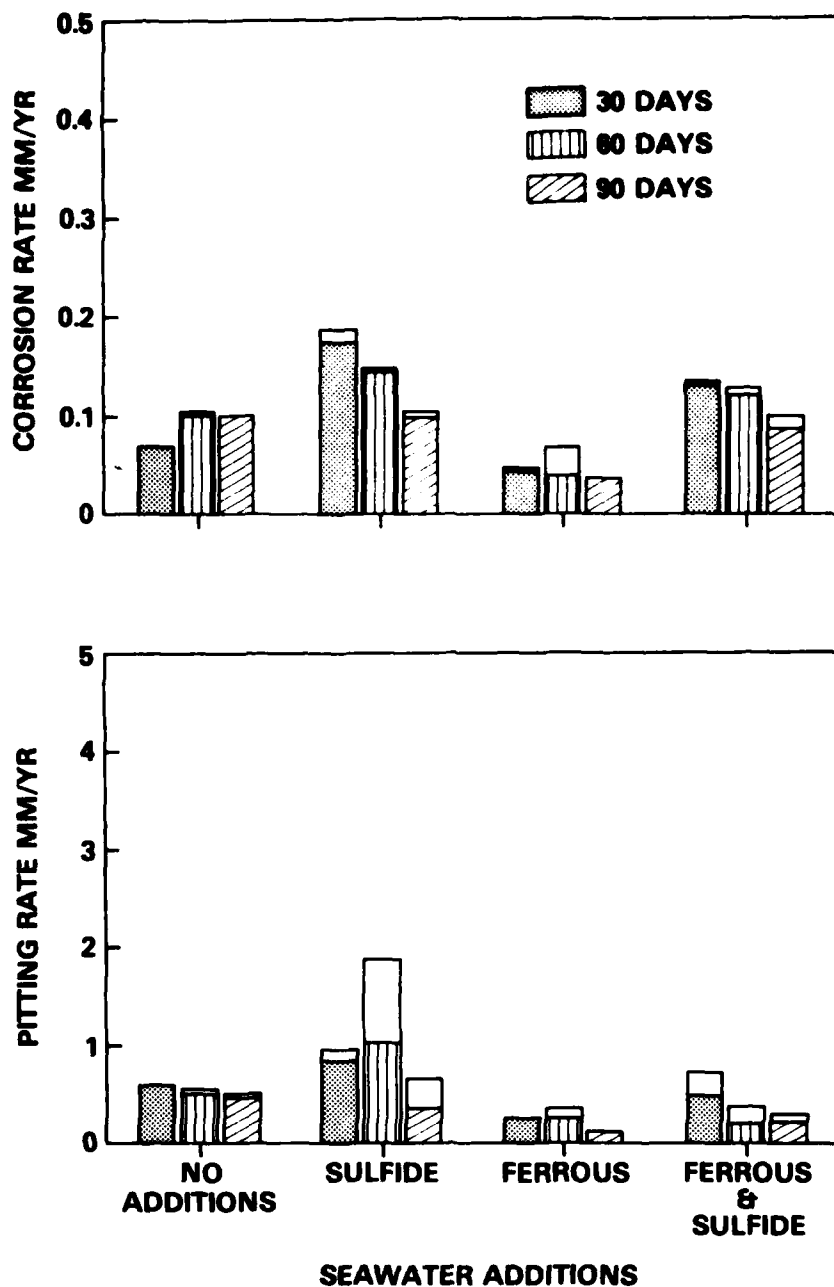


Figure 2 - Corrosion and Pitting Rates of Alloy C70600
Exposed to Seawater with Additions of Sulfide
(0.05 Milligram Per Liter) and/or Ferrous
(0.1 Milligram Per Liter) Ions

ALLOY C71500

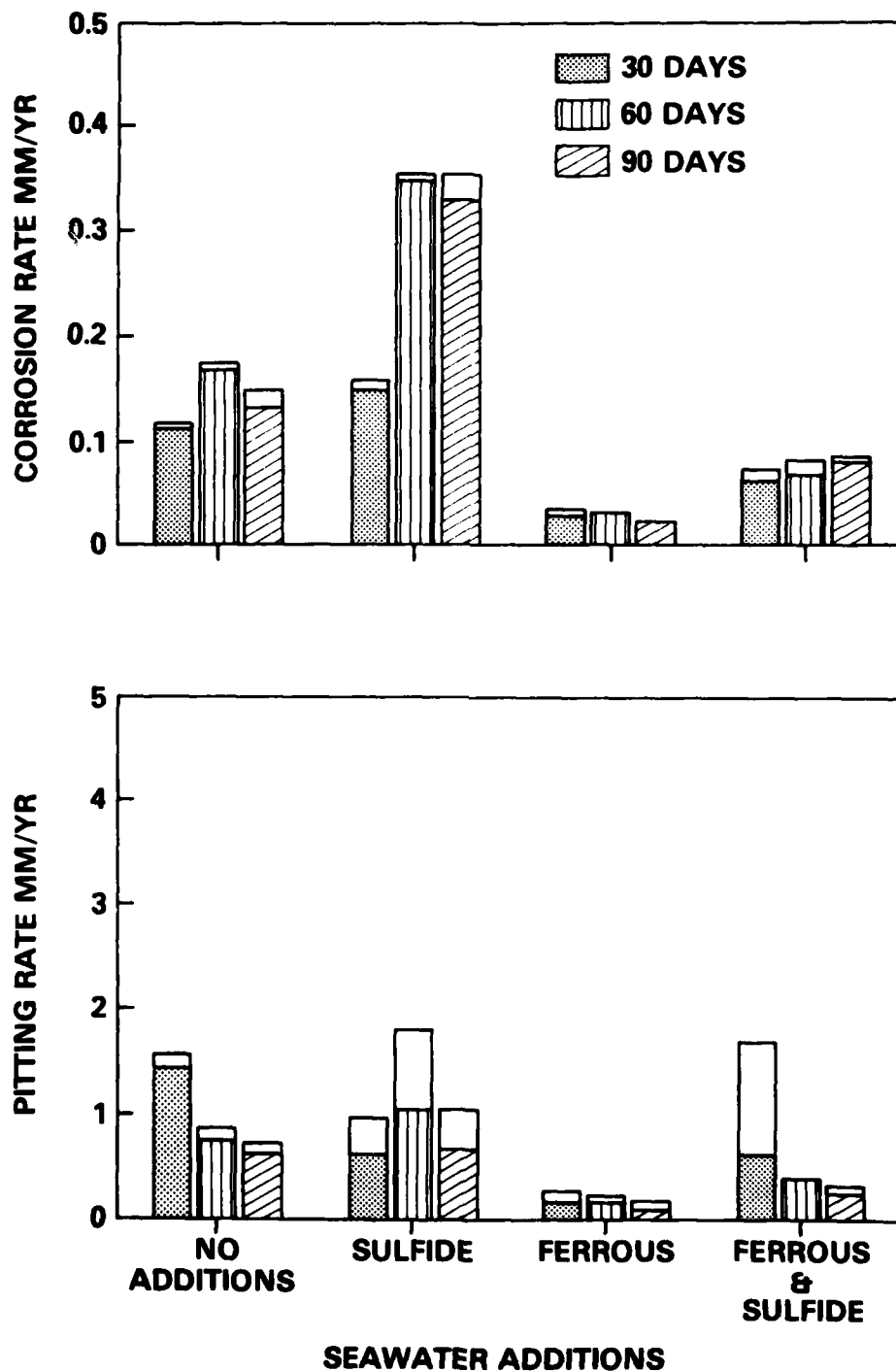


Figure 3 - Corrosion and Pitting Rates of Alloy C71500 Exposed to Seawater with Additions of Sulfide (0.05 Milligram Per Liter) and/or Ferrous (0.1 Milligram Per Liter) Ions

ALLOY C72200

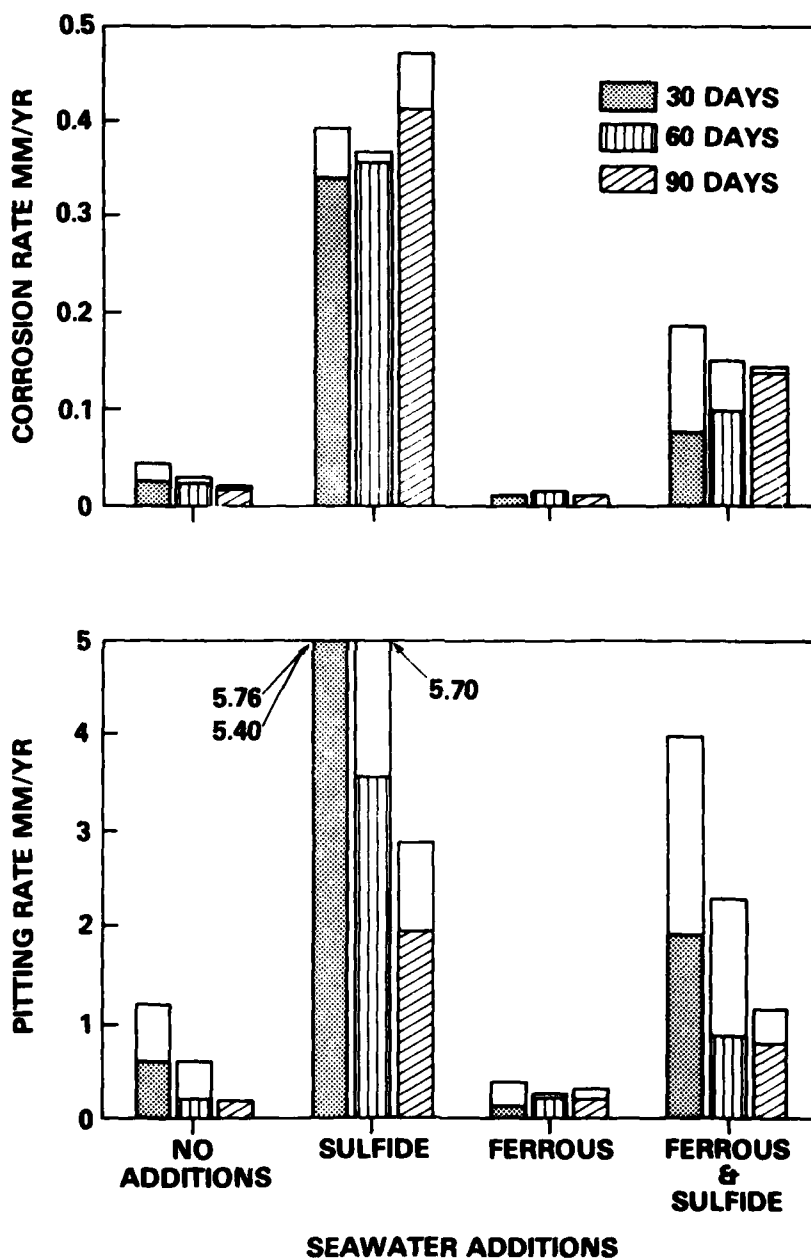


Figure 4 - Corrosion and Pitting Rates of Alloy C72200
Exposed to Seawater With Additions of Sulfide
(0.05 Milligram Per Liter) and/or Ferrous
(0.1 Milligram Per Liter) Ions

ALLOY C68700

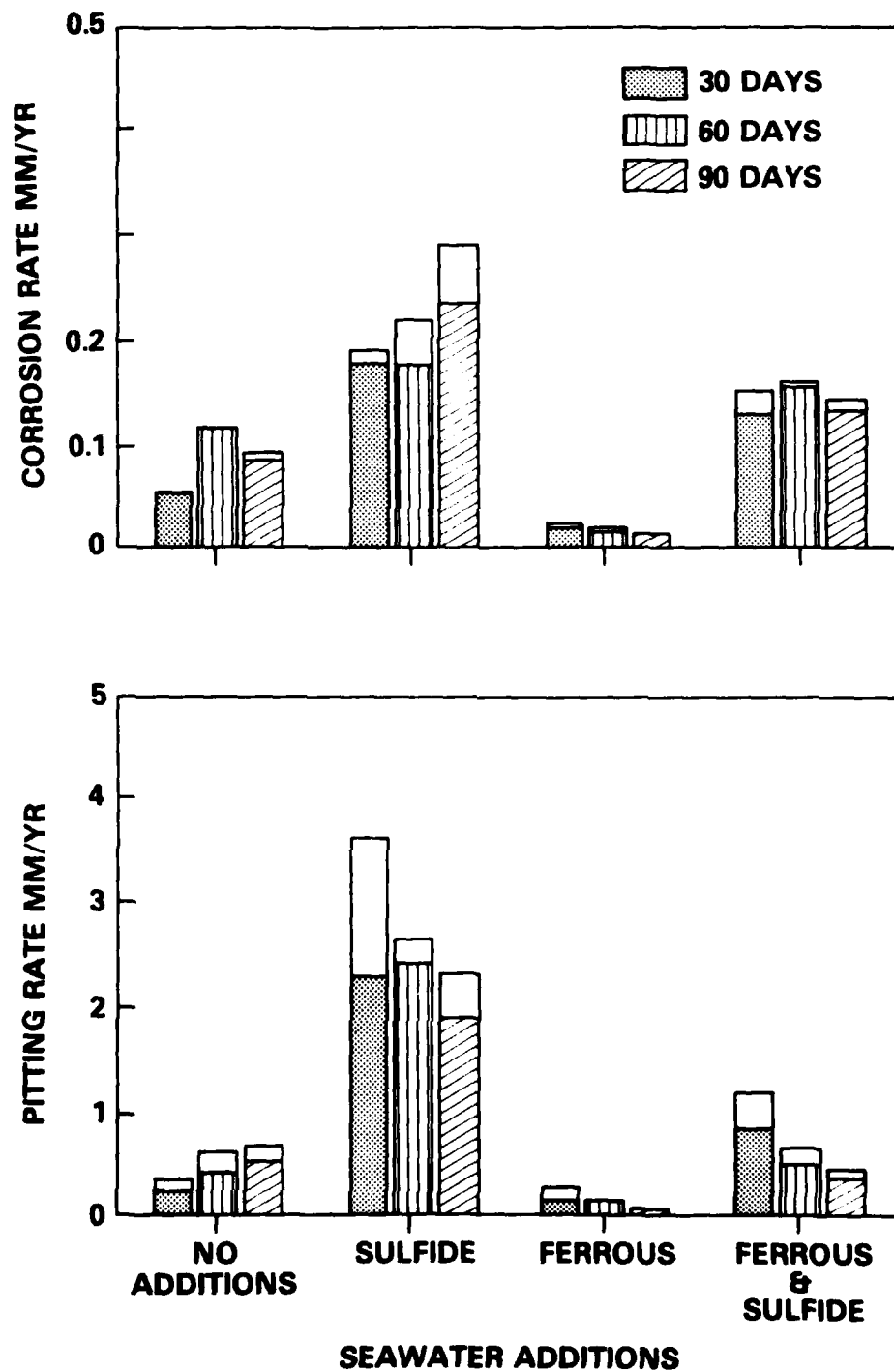


Figure 5 - Corrosion and Pitting Rates of Alloy C68700 Exposed to Seawater With Additions of Sulfide (0.05 Milligram Per Liter) and/or Ferrous (0.1 Milligram Per Liter) Ions

Data for Alloy C70600 (90-10 Cu-Ni) are presented in Figure 2. Corrosion and pitting rates stabilized or diminished after 60 days exposure, although the trend before this time was inconsistent. The addition of sulfide increased both corrosion and pitting rates, while the addition of ferrous ions decreased the rates. This is in agreement with previous studies.²⁰ The use of ferrous ions simultaneously with sulfide ions resulted in pitting rates no higher than those of the controls (no additions), and in corrosion rates no higher than those of the controls for the 90-day exposure period. Thus, given sufficient time, the ferrous ion additions suppressed sulfide-induced corrosion of this alloy.

Exposure results for Alloy C71500 (70-30 Cu-Ni) are presented in Figure 3. No effect of exposure time on the corrosion rates was evident, however, pitting rates tended to decrease with time. Sulfide additions to the seawater increased corrosion rates but had no significant effect on pitting rates. Ferrous ion additions dramatically decreased both corrosion and pitting rates. The ferrous addition completely suppressed sulfide-induced corrosion of this alloy under all exposure conditions. The use of ferrous sulfate was more effective in controlling general corrosion and sulfide-induced general corrosion of Alloy C71500 than of C70600, an observation also noted in a previous study.²³

Figure 4 illustrates the exposure results for Alloy C72200 (85-15 Cu-Ni plus chromium). An increase in exposure time had no effect on the corrosion rate of this alloy, although pitting rates were reduced at the longer times. The addition of sulfide resulted in a significant increase in corrosion and pitting rates, while the addition of ferrous ions had a smaller and opposite effect. Thus, the addition of the ferrous ions, although having some positive effects on corrosion, was not sufficient to completely suppress sulfide-induced corrosion of this alloy.

The corrosion behavior of Alloy C68700 (aluminum brass) is illustrated in Figure 5. The corrosion rate of this alloy tended to slightly increase with time when ferrous ions were absent, and tended to remain constant when ferrous ions were present. The pitting rate increased slightly with exposure time in the absence of ferrous ions and decreased with time in their presence. This suggests that the inhibitive effects of the ferrous ions on the corrosion of this alloy increase with time. Addition of sulfide increased both corrosion and pitting rates, while addition of ferrous ions decreased these rates. For all exposure periods the ferrous ion addition completely suppressed sulfide-induced corrosion.

DISCUSSION

No significant mechanistic research appears to have been conducted on the nature of inhibition of sulfide-induced corrosion through use of iron additions to the seawater. It is plausible to assume that one or both of two possible mechanisms exist in this process.

The previously described process of electrophoretic transfer of $\gamma\text{-FeO}\cdot\text{OH}$ to a filmed surface may still be operative depending upon the exact nature of the surface film formed in the presence of sulfide. The formation of a highly cathodic sulfide film or sulfide-modified oxide could provide an enhanced driving force for the deposition of the lepidocrocite film and a subsequent diffusion rate controlling process similar to that proposed by Epler and Castle¹⁶ for aluminum brass in clean seawater. That this mechanism may be at least partially operative is supported by previous research by Hack and Gudas,²⁴ where iron additions to seawater after exposure to sulfide-containing seawater resulted in some inhibition of corrosion.

A second mechanism of protection may result from the complexing of sulfide ions in seawater with the added iron where both are simultaneously present.^{8,23,30} The precipitation of a flocculent ferrous sulfide may serve to render the otherwise corrosive sulfide inactive. As pointed out by Syrett,³⁰ however, the quantity of ferrous sulfate added to seawater would have to be sufficient to complex the anticipated level of sulfide in the seawater.

In the use of ferrous sulfate or stimulated iron anodes to counteract sulfide-induced corrosion, an additional factor should be considered as it affects heat exchanger efficiency. As has been observed by others, the continued use of an iron addition technique can result in the buildup of a significant scale on the tube surface. At high enough levels of iron addition, sufficient sludge or precipitate may develop to result in complete blockage of the heat exchanger tubes.²³ At lower levels of iron addition, a bulky deposit will develop on the tube surface which may also interfere with heat transfer. Sato²⁵ studied the increase in deposit formation and loss of heat transfer for aluminum brass in seawater with both intermittent and continuous ferrous ion dosing. He recommended that some consideration be given to a gradual reduction in dosing levels after the initial film formation. Gasparini, et al,¹⁵ rationalized the existence of a bulky deposit after continued ferrous dosing based on the changing zeta potential characteristics of the surface and the reduced attraction of the colloidal $\gamma\text{-FeO}\cdot\text{OH}$ particles. They also suggested that a reduced level of dosing may be possible after the initial film formation.

In the current work, scale or deposit formation was evident on specimens exposed to the ferrous dosing as well as the simultaneous ferrous and sulfide dosing. In the latter case, the scale appeared no more extensive than when sulfide alone was injected into the seawater. The quantitative effects of this scale on heat transfer could not be assessed in the current work but it would likely contribute to a reduced heat transfer. Further studies will be necessary to optimize the level and rate of iron dosing from both corrosion and heat transfer considerations.

CONCLUSIONS

1. Alloy C70600 suffered sulfide-induced corrosion. Addition of ferrous sulfate reduced this corrosion, but a full 90 days was necessary for the effect of the ferrous sulfate to completely counteract the effect of sulfide.
2. Alloy C71500 suffered sulfide-induced general corrosion, but localized attack was not affected by sulfide addition. Addition of ferrous sulfate resulted in a significant decrease in the amount of corrosion and completely counteracted the sulfide-induced attack.
3. Alloy C72200 suffered greater sulfide-induced attack than the other alloys in the study. Addition of ferrous sulfate decreased the corrosion of this alloy somewhat, but was not sufficient at the level utilized to completely counteract the effects of the sulfide additions.
4. Alloy C68700 suffered sulfide-induced corrosion. Addition of ferrous sulfate decreased corrosion of this alloy but 90 days duration was necessary for the ferrous sulfate to mitigate the effect of sulfide.

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